ENVIRON

Comments on PCB Bioaccumulation Factors (BAFs) Developed by DRBC for Calculation of Water Quality Criteria (WQC) for the Delaware Estuary

September 20, 2004

ENVIRON has reviewed the derivation of the bioaccumulation factors (BAFs) currently being used by the Delaware River Basin Commission (DRBC) in the calculation of proposed water quality criteria (WQC) for total PCBs in the Delaware Estuary. Our review has included DRBC's summary table entitled "Revised Water Quality Criteria for Total PCBs, Delaware River Basin Commission", dated July 15, 2004, and spreadsheets of DRBC's BAF calculations based on fish tissue data collected in the fall of 2001 and the spring of 2002. We have also conducted an initial review of a report entitled "Bioaccumulation of Polychlorinated Biphenyls in the Delaware River Estuary," dated January 15, 2004, which is available on the DRBC website and apparently presents the underlying fish tissue data used in the DRBC spreadsheet calculations.

ENVIRON notes that only very limited documentation is provided regarding the technical basis for the bioaccumulation factors used by DRBC in calculating the revised water quality criteria. The DRBC summary table and spreadsheets do not present the technical rationale for the overall approach adopted for determining the PCB bioaccumulation factors, or provide the derivation for the critical input parameters, such as PCB concentrations in the water column, particle-bound organic carbon (POC) and dissolved organic carbon (DOC) concentrations in the water column, and lipid content of fish (whole or filet)[1]. In addition, the source of the PCB concentrations in fish tissue is not explicitly identified, although ENVIRON assumes that the data were derived from the January 15, 2004 "Bioaccumulation of Polychlorinated Biphenyls in the Delaware River Estuary" report. (Preliminary comments prepared by Coalition reviewers on this report are provided as Attachment A).

ENVIRON recommends that DRBC fully document the technical basis for the proposed bioaccumulation factors. Given the current lack of such full documentation, the comments summarized below should be considered preliminary.

[1] The July 15, 2004 "Revised Water Quality Criteria for Total PCBs, Delaware River Basin Commission" summary table identifies the source of the water column concentrations as data collected by DRBC in September 2001, and the lipid values as derived from an estuary database of fillet samples and a consumption study conducted by Penn State University. However, the estimation or selection of specific values from these sources for use in the BAF calculation is not documented in the materials provided.

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ENVIRON's preliminary comments are summarized below:

1. Use of the BAF values represents a highly simplified approach that does not reflect the complexities of the bioaccumulation process. Application of BAF values in bioaccumulation calculations and the development of WQC is based on an assumption that there is a direct, linear relationship between PCB concentrations in water and fish tissue, and that this relationship remains invariant over time, space, and the concentration range of interest. In reality, such a relationship has not been demonstrated for PCBs in the Delaware estuary and in all likelihood does not exist. This is particularly true given the very low solubility and high affinity to sediments exhibited by PCBs, making estimation of PCB concentrations in the water column (particularly in dissolved form) extremely difficult and highly uncertain.

   The uncertainty of attempting to characterize the bioaccumulation process is illustrated by the analytical results of fish tissue samples collected from channel catfish (selected by DRBC to represent trophic level 3 species) and white perch (selected by DRBC to represent trophic level 4 species). Based on theoretical considerations as described in USEPA's "Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health" (USEPA 2000), the PCB BAF value on a lipid basis would be predicted to be higher in the trophic level 4 species than in the trophic level 3 species, due to biomagnification up the food chain. However, the data collected for channel catfish and white perch from the Delaware estuary indicate an opposite trend[2]. This is likely due to the bottom-feeding behavior of catfish, which increases its exposure to PCBs in sediment.

   Such results demonstrate that a simplistic treatment of the bioaccumulation process, such as is inherent to the BAF approach, can lead to significant error. As stated in "Bioaccumulation of Polychlorinated Biphenyls in the Delaware River Estuary," dated January 15, 2004 (p.i):

   > "There was considerable variation in t-PCB [total PCB] concentrations for individual catfish and perch fillets with a region of a zone. These differences were not significantly reduced upon lipid normalization of t-PCB concentrations suggesting that within a zone, there may be many factors driving accumulation such as dietary shifts, small-scale (within zones) heterogeneity in sediment concentration, and non-equilibrium conditions in contaminant partitioning."

   The BAFs estimated by DRBC are best interpreted as a simple regulatory tool rather than as scientifically defensible values that allow for an accurate prediction of how changes in

[2] DRBC did not consider any data on accumulation of PCBs in striped bass, a key target fish for anglers along the Delaware River according to the March 31 2004 report entitled "Patterns of Sport Fish Consumption at Six Pennsylvania Sites Along the Tidal Portion of the Delaware River with Special Emphasis on Shore Anglers". It is not clear that the data for white perch or channel catfish are representative for striped bass or other species, given the lack of agreement of the data with results anticipated strictly based on considerations of trophic level alone.

PCB concentrations in the water column will effect PCB concentrations in fish tissue. ENVIRON understands that DRBC has received a proposal to develop a food web model from the authors of the "Bioaccumulation of Polychlorinated Biphenyls in the Delaware River Estuary". If DRBC believes that it must develop a WQC for total PCBs to support the TMDL process, DRBC should utilize a such food web model rather than BAFs, unless it can be demonstrated that PCB concentrations in fish tissue in the Delaware Estuary are linearly related to concentrations in the water column and that the relationship remains invariant over the concentration range of interest. Otherwise, the WQC may not represent an effective goal for TMDL implementation.

2. The BAFs derived by DRBC are most applicable to the penta- and hexa- PCB homologs, and are increasingly unreliable as the homologs become more or less chlorinated. DRBC should explicitly account for the differences between the congeners and homologs in developing appropriate water quality goals. Given its objective of developing WQC for total PCBs (PCB_t), DRBC does not attempt to calculate BAFs for individual congeners or homologs even though such data are available from the 2001 and 2002 fish tissue analyses. As a result, the BAF calculations rely on averaging of data even though there is significant variability in properties across homologs and even across congeners within a homolog. For example, as indicated in the DRBC spreadsheets, the calculated hypothetical freely dissolved fraction (f_d) of PCBs ranges from more than 90% for the mono-homolog to 0.3% for the deca-homolog, and yet the WQC is based on a single hypothetical f_d value of 12%. As calculated by DRBC, this value does not explicitly take into account the homolog (or congener) distribution in either fish tissue or the water column. An alternative approach would be to develop separate BAF values for the individual congeners (or, at a minimum, the various homologs). These values could then be used in combination to calculate a BAF value that reflects a specific congener or homolog distribution of interest.

   ENVIRON understands that the water quality model for PCBs in the Delaware Estuary is being developed by DRBC on a homolog-specific basis, in recognition of the important differences between the various homologs. For the same reason, and for consistency with the water quality model, the bioaccumulation of PCBs in the food web should also take into account differences between congeners and homologs.

3. DRBC should provide documentation for the estimated PCB, POC and DOC concentrations in the water column. These parameters are critical input factors in the BAF calculation. The source of the "Total Water Concentration" data used to derive the "Measured BAF" in the DRBC spreadsheets is not provided, and thus the reliability and reproducibility of these data cannot be evaluated. It appears that the total PCB concentration corresponds to the analysis of water in which particulate matter is present, and thus the measured PCB concentrations reflect both dissolved and particle-bound PCBs. The dissolved fraction of PCBs in the water column, which is a critical factor in the BAF calculation, is estimated using a model that does not appear to have been validated. Furthermore, the source of the key input data to this model (i.e., POC and DOC) is not documented in the materials provided. Therefore, it is not clear to what extent the POC and DOC values assumed for each estuary zone in the BAF calculations

are consistent with the POC and DOC values in the actual water samples used for PCB analysis or what steps, if any, were taken to control particle levels in the samples so that PCB concentration measurements are comparable.

4. DRBC should provide documentation for the assumed values of "% lipid in consumed fish" used in the BAF calculations. DRBC properly adjusts the calculated BAFs to account for the reduced lipid content of consumed fillets, as opposed to whole fish. For example, a lipid content of 3.87% is used for trophic level 3 fish (compared to an average measured lipid content between 8% and 9% in sampled channel catfish) and a lipid content of 2.48% is used for trophic level 4 fish (compared to an average measured lipid content of about 7% in sampled white perch). The bases for these "% lipid in consumed fish" values have presumably been derived from the 2001 and 2002 sampling events in the Delaware estuary, but have not been provided. It is important the values used in the BAF calculation reflect the species consumed and preparation habits for the target fish-eating population.

5. DRBC should confirm that treatment of data in the evaluation of bioaccumulation potential is consistent with data treatment in the development of the PCB water quality model for the Delaware Estuary. Treatment of data (e.g., handling of non-detects, J values, methods for combining congener data, etc.) in the development of a water quality standard should carry through to the development of source loads and other water quality model inputs. Analytical methods used in developing the data should also consistent where applicable, and the MLD and PQL values for each data set presented.

Please feel free to give me a call if you have any questions.

Attachment A

Preliminary Comments on
"Bioaccumulation of Polychlorinated Biphenyls in the Delaware River Estuary"
Report No. 03-03F

General Comments

- The rationale for using composited whole fish and fillet tissue data, instead of individual fish tissue data, should be discussed and its impact on the statistical analysis explained.
- The size and age of fish can have profound effects on the magnitude and variability of PCB concentrations in tissue residues, and should be taken into account in evaluating the bioaccumulation results. All of the statistical analyses and results by species and zone would likely be changed if the analyses were based on fish tissue residues standardized for fish size/age.
- The ambient water data used to calculate BCFs, BSAFs and PPRs in the report are not provided or discussed. Detail is required regarding how the estimated water concentrations were determined (e.g., methods for PCB analysis, water sample collection equipment and techniques, whole water samples, filtered water samples, etc.).
- Given the way the fish PCB tissue residues were determined (e.g., composited samples) and the fact that the study is evaluating PCB congeners with vastly different physical-chemical properties, the concept of, or calculation of, a "universal" log BCF value of 7 for the Delaware system is not supported by the study.

Specific Comments

p. 5 It is unclear how fish were prepared for subsequent chemical analysis. No mention is made of how fish were processed (e.g., whole fish, fillets with skin on or off, did whole fish processing include stomach contents or were these removed, etc.). Critical information regarding sample sizes and sample homogenization techniques is not provided. In addition, no information is presented on the length of time allowed for invertebrate gut purging or the effectiveness of the purging procedure.

p. 5 It is unclear if lipids were measured on samples of whole fish, fillets, or both. No description is provided of the actual procedure used for the lipid analysis other than that it was a "gravitmetric analysis".

p. 5 In the section on PCB congener analyses, it is unclear why the method of Mullin (1985) was used for congener analyses when other, more recent methods are available.

p. 6 The report indicates that concentrations below the instrumental detection limit were assigned a value of 0.01 for the statistical analysis using PCA. What was the range of instrument detection limits, and what effect did the assumption regarding non-detect values have on the statistical analysis? In addition, the report indicates that congeners that were "consistently" ranked as non-detect were not considered in the statistical analysis. What criteria were used to determine when to eliminate a congener from the analysis?

This section indicates that PCA was conducted on whole fish data but should actually indicate that PCA was conducted on data only for *composited* whole fish.

p.8, para 1 In the discussion of the data summarization process and Tables A1-A21 in Appendix 1, it is unclear how the 0.01 values that were substituted for values that were below the instrumental detection limits (see previous comment) were handled or indicated in the tables. The various descriptions for analytical qualifiers on data, e.g., ND, BDL, method detection limit, analytical detection limit, instrumental detection limit, should be defined somewhere in the report and used in a more rigorous manner in the text. It would also be useful to know the general relationship between the DL (as used in BDL) and the LOQ and how they were determined.

p. 8, para. 3 This paragraph discusses summing the composite fillet and composite "remains" total PCB values to determine a (composite?) whole fish total PCB value. The use of "remains" is not explained, nor is the procedure for separating fish into fillet and "remains". This issue also leads to questions about how lipids were determined (e.g., were they determined on composited fillet and composited remains and summed to produce (composite) whole fish lipids concentrations?) Was the variability of lipid content also assessed in the "variability" study?

p. 8 It is inappropriate to estimate total PCB values for "remains" and subsequently whole fish in the manner described in paragraph 3 for the 2 samples of remains (and consequently, whole fish) that were lost for Zone 2 fall and Zone 4 spring white perch. These results should be excluded.

p. 8, para 4 The treatment of the spring Zone 5 catfish data (i.e., "transformation" to meet CBL average recoveries from all samples of 90%) seems inappropriate given the fact that other total PCB values were not corrected for surrogate loss. Based on the justification provided for this operation (i.e., surrogate correction for low surrogate recoveries of SRMs increased accuracy) it would seem that accuracy of all sample analyses would be increased by correction for surrogate loss.

p. 9 In the section on "Core Studies", the discussion of the variability in tissue residues indicates that the variability is fairly unremarkable (e.g., a factor of 4 – 5X). This is particularly true given the fact that the data were not standardized for the size (e.g., length) or age of the fish. The report itself indicates that the variability in fish weight and age was from 27 – 220 g and 2- 9 years of age for white perch and 129 – 2170 g and 3 – 19 years for catfish. This variability in size and age can have profound effects of tissue residues of PCBs and their variability but no discussion is provided on this topic. Better segregation of fish by age/size would also provide better information on longitudinal trends in tissue residues.

p. 10 The discussion of the "tremendous" variability in catfish PCB tissue residues and the variability in white perch tissue residues should be supported by an evaluation in which the tissue data are standardized for the age/size of the catfish and white perch.

p. 11 In the section on PCA, it is indicated that PC 1 and PC2 account for 52% of the variance (assumed to be a results of 37% for PC1 plus 15% for PC2). However, it appears that PC2 actually accounts for 15% of the residual variance, i.e., 15% of 63% (100% minus 37%) = 9.5% for PC2 or 46% for PC1 and PC2 combined.

p. 14 The report does not provide a basis for the statement that the truly dissolved phase for total PCBs is on average 18% of the filtrate concentrations. The supposed increase in BCF with Kow is also t weak given that the R values for figures 40-43 were all less than 0.44. "Most" BCF calculations in the literature are from laboratory (not field) studies so colloids are likely not an issue and "most" BCF values are not underestimated. In contrast, most field studies typically estimate BAF or BSAF values.

p. 15 The significance value be ($P<0.001$), not ($P>0.001$). Also, this value does not agree with Figures 40 – 43, where the P values is indicated to be ($P<0.0001$).

p. 15 The text of the first full paragraph indicates that the parabolic function better explains the relationship between the Kow and the BSAF. While this may be true, in fact no simple relationship was demonstrated based on the very low R values (less than 0.20, including those for the parabolic function).

p. 15 Differences in tissue residues between catfish and white perch are also likely to be related the size/age of the fish. The variability in age/size was much greater for catfish than for the white perch.

p. 15 The greater BSAF values calculated for the Delaware may also be due to differences in analysis of fish (i.e., development of tissue residue data) and the quality of the data used for calculation of the BSAF values.